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Alloying-Driven Phase Stability in Group-VB Transition Metals under Compression

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Abstract. The change in phase stability of Group-VB transition metals (V, Nb, and Ta) due to pressure and alloying is explored by means of first-principles electronic-structure calculations. It is shown that under compression stabilization or destabilization of the ground-state body-centered cubic (bcc) phase of the metal is mainly dictated by the band-structure energy. In the case of alloying the change in phase stability is defined by the interplay between the band-structure and Madelung energies. We show that band-structure effects determine phase stability when a particular Group-VB metal is alloyed with its nearest neighbors within the same *d*-transition series: the neighbor with less and more *d* electrons destabilize and stabilize the bcc phase, respectively. When V is alloyed with neighbors of a higher (4*d*- or 5*d*-) transition series, both electrostatic Madelung and band-structure energies stabilize the bcc phase. Utilizing the self-consistent *ab initio* lattice dynamics approach, we show that pressure-induced mechanical instability of bcc V, which results in formation of a rhombohedral (rh) phase at around 60-70 GPa at room temperatures, will prevail significant heating and compression. Furthermore, alloying with Cr decreases the temperature at which stabilization of the bcc phase occurs at elevated pressure.

Introduction

Vanadium metal has seen a surge in research, experimental and theoretical, driven mainly by its importance in applications but also because of its surprising destabilization of the bcc ground-state phase close to 60 GPa. On the experimental side, synchrotron x-ray diffraction measurements [1] reported a novel rh phase that is a relatively small distortion of bcc phase in vanadium metal around 63-69 GPa.

Theoretically, the bcc → rh transition has been confirmed by the electronic-structure study [2] that also predicts the bcc phase to re-enter above 300 GPa. It has been proposed that intra-band Fermi-surface (FS) nesting is responsible for the instability of the cubic phase of vanadium metal under compression [3,4] that appears to be associated with a substantial pressure-induced softening of the shear elastic constant, C_{44}.

The main task of this paper is to study stability of Group-VB transition metals due to alloying with a small amount of a neighboring metal, particularly stabilization or destabilization of the bcc phase relative to a lower symmetry rh phase under compression. Also, even though the existence of the intra-band FS nesting in vanadium metal is widely acknowledged, it has repeatedly been argued in the literature [2,4] that the softening of C_{44} will disappear at higher temperatures because the rhombohedral distortion is very small and elevated temperatures would washout the destabilization of the bcc phase and thus removing the bcc → rh transformation. Thus, another purpose of our study is to clarify if indeed high temperatures expand the bcc stability field in the vanadium phase diagram. We also address the influence of alloying on the stability of the bcc phase of vanadium metal at elevated pressures and finite temperatures.

Our paper is organiazed as follows. Pertinent detailes of methodlogy are given in the next section folowed by results on stability of the bcc alloys based on V, Nb, and Ta. The separate section is dedicated to study of vanadium metal and V-Cr alloys at elevated temperatures. Finally we present conclusions.

Computational details

The calculations that we have referred to as exact muffin-tin orbitals (EMTO) are performed using a scalar-relativistic Green function technique based on an improved screened Korringa-Kohn-Rostoker method [5]. For the exchange/correlation approximation, we use the generalized gradient approximation (GGA) [6]. In order to treat compositional disorder the EMTO method is combined with the coherent potential approximation (CPA) [7,8]. Integration over the irreducible wedge of the Brillouin zone is performed using the special *k*-points technique [9]. These calculations include the on-site screened Coulomb potential and energy, which take care of the electrostatics in the single-site CPA approximation [10]. The corresponding screening constants have been obtained in the locally self-consistent Green function (LSGF) [11] calculations for a 1024 atoms supercell that models the random equiatomic alloys.

For the elemental Group-VB metals, the calculations are also performed using a full-potential linear muffin-tin orbital method (FPLMTO) [12] with the same choice (GGA) for the exchange/correlation. In order to study disordered alloy within FPLMTO we conveniently apply the virtual crystal approximation (VCA) that is usually applicable and appropriate when alloying metals that are neighbors in the Periodic Table.The equilibrium density and EOS are obtained from a Murnaghan fit [13] to the total-energy versus the lattice constant curve. For the determination of the trigonal shear elastic constant, C_{44}, we apply a volume-conserving monoclinic distortion [14] and calculate the internal energy response. The ground state for the rh phase is obtained by applying a volume conserving rhombohedral distortion [2].

For the V-Cr alloys we apply a scheme to take phonon-phonon interactions into account at elevated temperatures namely the self-consistent *ab initio* lattice dynamics (SCAILD) method. This approach is described in great detail [15]. The forces needed for the SCAILD methodology are obtained from electronic-structure calculations performed within FPLMTO-VCA formalism.

Stability of the bcc alloys based on the V, Nb, and Ta

Fig. 1 shows calculated (FPLMTO, [16]) pressure dependence of the trigonal shear elastic constant, C_{44}, in V, Nb, and Ta. For V we predict the phase transition to the rh phase at 0.6 Mbar, close to the observed 0.6-0.7 Mbar [1]. For Nb the shear constant reaches a low minimum close to 0.5 Mbar before rising again. In Ta the softening is less severe but apparent between 0.5-0.8 Mbar.

In Fig. 2 we display the total energy (EMTO-CPA. [16]) as a function of rhombohedral distortion for V and its alloys with 5 at. % of Ti, Cr, and Nb. Here the atomic volume is kept at Ω = 8.056 Å^3 corresponding to a pressure of ~ 2.4 Mbar. According to EMTO-CPA calculations [3, 4], this pressure corresponds to the point of the maximum stability of the rh phase of pure V in respect with the bcc phase – the ground state phase at ambient pressure. Notice that pure V is unstable with respect to the distortion and alloying with a small amount of its left neighbor Ti increases the instability. Adding a small fraction of Cr or Nb, however, promotes the bcc phase which becomes stable for ~ 5 at. % Nb and ~ 11 at. % Cr (not shown in Fig. 2). Our calculations [17] also show that a small (~ 3-5 at. %) amount of 4*d*- (Zr, Mo) or 5*d*- (Hf, Ta, W) metals stabilizes the bcc phase of vanadium metal at all pressures.

Within the EMTO formalism, the total-energy, E_{tot}, can be expressed as the sum of two contributions: $E_{tot} = E_1 + E_M$, where E_1 consists of all "local" (band-structure) contributions, $E_1 = E_s + E_{intra} + E_{xc}$, such as the kinetic energy of non-interacting electron gas, E_s, the intra-cell electrostatic energy, E_{intra}, which is due to the electron-electron and electron-ion Coulomb interactions and also includes the screened Coulomb interactions in the case of the DFT-CPA calculations, and the exchange and correlation energy, E_{xc}. The remaining contribution, E_M, is the inter-cell Madelung energy.

Table 1 lists the total-energy response ΔE_{tot} and its contributions, ΔE_1 and ΔE_M to a 1 % monoclinic deformation, used for the shear elastic constant C_{44} calculations, calculated for V and the $V_{95}Nb_{05}$, $V_{95}Ti_{05}$, and $V_{95}Cr_{05}$ alloys at the atomic volume Ω = 8.056 Å^3. Negative values of the total-energy changes indicate mechanical instability of the bcc phase. Adding Nb to V significantly increases ΔE_{tot} thus indicating stabilization of the bcc structure in the $V_{95}Nb_{05}$ alloy.

Notice that the increase of ΔE_1, which is mostly due to band-structure effects, is rather insignificant and the main reason for stabilization of the bcc structure in the $V_{95}Nb_{05}$ alloy is instead the electrostatic Madelung energy ΔE_M. V alloyed with Ti reacts differently. Here ΔE_{tot} decreases signaling a further bcc destabilization. However, contrary to the V-Nb system, the change in E_1 plays the dominant role while ΔE_M remains nearly constant. Finally, for the $V_{95}Cr_{05}$ alloy, again the band energy is dominant, now having the opposite effect while the Madelung part remains nearly the same. Consequently, ΔE_{tot} increases and approaches zero with a near stabilization of the bcc phase. Adding an additional 6 at. % of Cr in fact dictates the bcc phase for all pressures in V.

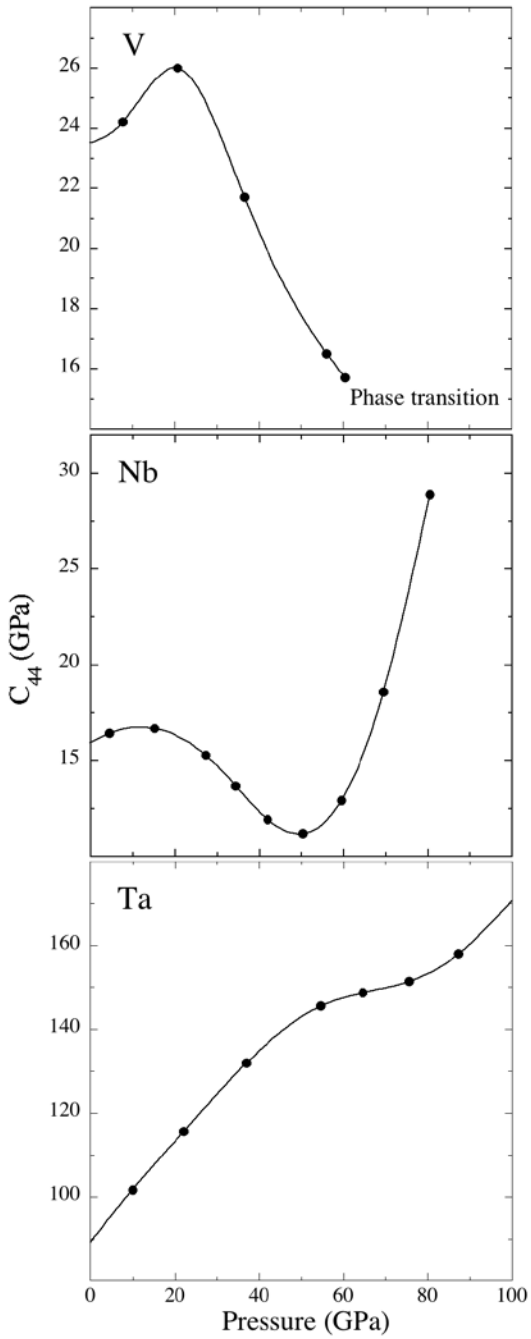

Fig. 1. Calculated (FPLMTO, [16]) pressure dependence of the shear elastic constant in V, Nb, Ta.

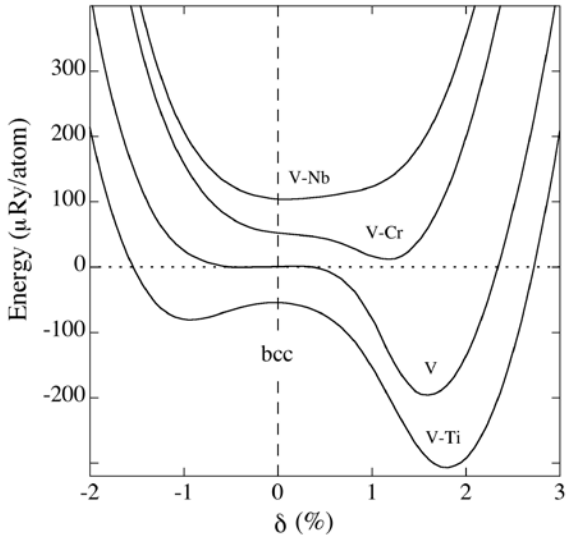

Fig. 2. Calculated (EMTO-CPA, [16]) total energy (at the atomic volume Ω = 8.056 Å^3) as a function of the rhombohedral deformation parameter δ (see Ref. [2] for explanation). The undistorted (δ = 0) crystal corresponds to the bcc phase. The curves for $V_{95}Ti_{05}$, $V_{95}Cr_{05}$, and $V_{95}Nb_{05}$ are shifted apart 50 mRy for a better display of the results.

Table 1. Contributions (EMTO-CPA, [16]) to the total-energy change (ΔE_{tot}) due to a 1 % monoclinic deformation for V, Nb, Ta and their alloys.

Material	ΔE_1 [mRy]	ΔE_M [mRy]	ΔE_{tot} [mRy]
V	-0.2010	0.1820	-0.0190
$V_{95}Nb_{05}$	-0.1951	0.2102	0.0151
$V_{95}Ti_{05}$	-0.2130	0.1895	-0.0235
$V_{95}Cr_{05}$	-0.1887	0.1823	-0.0064
Nb	-0.0860	0.1930	0.1070
$Nb_{95}Zr_{05}$	-0.1200	0.1881	0.0681
$Nb_{95}Mo_{05}$	-0.0808	0.1910	0.1102
Ta	-0.0080	0.2250	0.2170
$Ta_{90}Hf_{10}$	-0.0170	0.2290	0.2120
$Ta_{90}W_{10}$	0.0000	0.2250	0.2250

The band energy is also responsible for the pressure-induced shear softening in Nb at ~ 50 GPa (Fig. 1). Hence, there is an interest to explore the stability of bcc Nb with alloying. Here we undertake calculations of the energy change of pure bcc Nb, and its alloys with 4*d* neighbors ($Nb_{95}Zr_{05}$, and $Nb_{95}Mo_{05}$) caused by 1 % of the monoclinic deformation. Calculations are performed at the atomic volume Ω = 14.92 Å^3 corresponding to a pressure of ~ 50 GPa and the results are presented in Table 1. There are obvious analogies to the case of V. Addition of (5 at. %) Zr to Nb decreases ΔE_{tot} due to the band-energy contribution but not quite enough to destabilize the bcc phase. When increasing the Zr content to 11 at. % in Nb, our calculation suggest a destabilization of the bcc phase at ~ 87 GPa (ΔE_{tot} becomes equal to zero) consistent with the scenario for Ti-doped V. Also, analogous to V, the Madelung contribution is rather insignificant while the change in the band energy is clearly driving the destabilization. Adding Mo to Nb causes the same effect that is observed in the V-Cr alloy: the band energy further favors the bcc phase while the Madelung contribution is inconsequential.

We perform calculations of the energy change of pure bcc Ta, and its alloys with 5*d* neighbors ($Ta_{90}Hf_{10}$, and $Ta_{95}W_{10}$) caused by 1 % of the monoclinic deformation. The calculations are performed at the atomic volume Ω = 14.68 Å^3 corresponding to a pressure of ~ 65 GPa, which is within the range of the C_{44} softening (Fig. 1) and the results are presented in Table 1. Again, there are analogies to the case of V and Nb. Addition of Hf (W) to Ta decreases (increases) ΔE_{tot} due to the corresponding change of the band energy part. Even though Hf in Ta have a destabilizing effect due to the band energy, the bcc phase always remains stable simply because the softening in C_{44} in Ta (Fig. 1) is not severe enough to promote a phase transition.

Stability vanadium metal and V-Cr alloys at elevated temperatures

Calculations described in previous section are performed at T = 0 K and temperature effects (lattice vibrations) are not accounted for. In this section the bcc phase stability is determined by computing the phonon dispersions as functions of temperature. The bcc phase stability for the V-Cr alloy system is studied for two atomic volumes (10.41 Å^3 and 8.58 Å^3) that correspond to zero-temperature pressures of 74 GPa and 182 GPa, respectively. These volumes are chosen because one represents the early onset of the rh phase and the other the maximum rh phase stability in terms of the bcc – rh energy difference [18]. We perform these simulations (FPLMTO-VCA) for bcc V and four bcc V-Cr alloys ($V_{95}Cr_{05}$, $V_{90}Cr_{10}$, $V_{85}Cr_{15}$, and $V_{80}Cr_{20}$) as a function of temperatures paying attention to the lowest temperature that stabilizes all phonons [18].

In Fig. 3 we display the mechanical-stability temperatures of bcc V and the four V-Cr alloys mentioned above. One realizes that addition of Cr to V decreases the temperature of stabilization of the bcc phase although in the case of the larger atomic volume this effect is less pronounced.

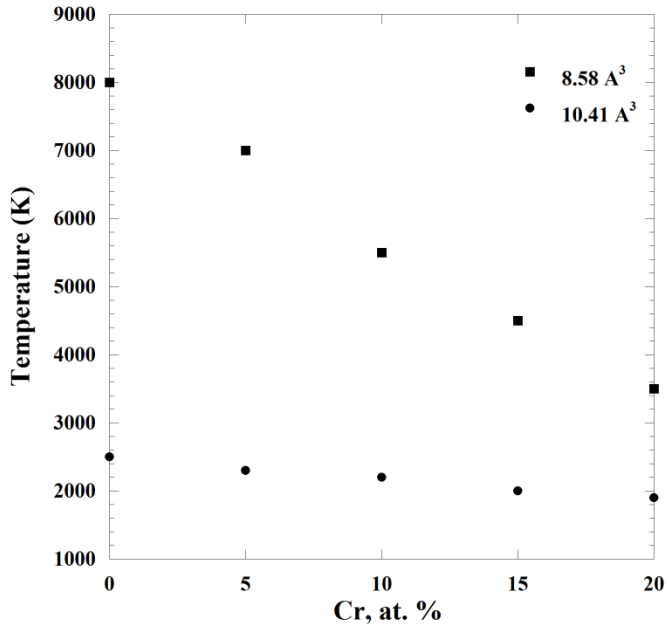

Fig. 3. Calculated (FPLMTO-VCA) temperature of mechanical stability of bcc V-Cr alloys at Ω = 10.41 Å^3 and Ω = 8.58 Å^3 [18].

Conclusions

We have identified softening in the shear elastic constant for the Group VB metals with pressure. For V the softening is associated with a transition to rh phase close to 60 GPa while for Nb and Ta the bcc phase still remains stable at all studied pressures. The effect of alloying on the phase stability has been studied and two dominant mechanisms (band and Madelung energies) are recognized. The band energy tends to destabilize (stabilize) the bcc phase when a member of the Group VB is alloyed with its nearest neighbor from the same *d*-transition series to the left (right).

Utilizing the self-consistent *ab initio* lattice dynamics approach, we show that pressure-induced mechanical instability of bcc V will prevail significant heating and compression. We find that the rh phase remains stable under heating up to ~ 2500 K at the early onset of the bcc to rh phase transition (Ω = 10.41 Å^3). The aforementioned temperature (~ 2500 K) of destabilization (stabilization) of the rh (bcc) phase is significantly below the shock melting temperature of the bcc vanadium, T_m ~ 4000 K, reported in Ref. [19] at ~ 75 GPa. Thus, we conclude that the transition to the rh phase in vanadium metal shall be exposed by DAC experiments at high temperatures (up to the upper temperature limit, ~ 2500 K that can be achieved by laser heating).

At the smaller volume (Ω = 8.58 Å^3), our model establishes 8000 K as an upper bound of stability of the vanadium rh phase with bcc phase taking over beyond that. This temperature, however, is clearly above the shock melting temperature, T_m ~ 6800 ± 800K at 182 GPa [19].

Alloying with Cr decreases the temperature at which stabilization of the bcc phase occurs.

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